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A REVIEW OF NOISE STUDIES IN SUPERIONIC ELECTROLYTES

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Abstract

This paper reviews electrical noise and its measurement in superionic solid electrolytes. The essential noise generation is associated with thermal agitation, diffusion and electrochemical reaction of mobile ions in the bulk superionic electrolyte and at interfacial contacts. Simulation calculations display the superposed patterns of different noise sources and their resolution. Recent experimental results on sodium β"alumina and Nasicon are presented.

INTRODUCTION

The study of electrical fluctuations in superionic, high conductivity solid electrolyte systems is of interest for several reasons:

1. The superionic solid is an ionic conductor in which the electrical current is accompanied by ion migration. Experimentally observed electrical noise reflects ion transport dynamics in the bulk material.

2. Nyquist or thermal agitation noise is determined by the conductance of the system. Its dependence upon temperature and frequency measures the activation energy and the capacitive nature of the bulk material and interfacial contact.

3. In equilibrium or non-equilibrium states, electrical fluctuations in both the presence and absence of current provide information about electrochemical reactions taking place within the electrolyte and the electrode and at the interface between them.

4. Variations in noise may be expected during a phase transition in the electrolyte material and degradation of electrolyte material or

device. Particularly, the noise examination can be conducted without additional electrical current or potential which is most desirous when the superionic solid to be investigated is susceptible to electrical damage.

5. Noise exists at the contacts or junctions made in ionic devices. Its measurement is of considerable importance in evaluating and improving the design and applications of practical devices.

The first reports concerning contact and current noise in superionic conductors was published by J. J. Brophy and coworkers[1,2] in 1983. This investigation examines voltage fluctuations in β" and β alumina in the presence and absence of current. Later, detailed studies have been reported on sodium[3] and silver[4] β"alumina and also extended to divalent substitutes[5] and Nasicon[6]. This paper reviews fluctuation studies conducted on superionic conductors, including a general description and experimental results on sodium β", β alumina and Nasicon. In the first two parts we describe briefly the basic fluctuations in superionic systems and measurement methods. The third part concerns simulation calculations that are considered helpful in analyzing multicomponent noise. Lastly an overview of more recent investigations on contact and current noise in sodium β"alumina-different ionic electrode systems and in Nasicon is presented. Most of the experimental results included in the last two parts have not yet been published.

BASIC FLUCTUATIONS IN SUPERIONIC CELLS

1. Nyquist or thermal noise[7], which always occurs in a non-zero resistance component above zero Kelvin temperature is expressed by

$$S_{Nyquist} = 4kTR\Delta f \qquad (1)$$

where R is the resistance of the component, Δf the measurement frequency bandwidth, k is Boltzmann's constant and T the Kelvin

temperature. From equation (1) we obtain white noise from a pure resistance. However, in a system including resistive and capacitive components, the R in equation (1) is replaced by the real part of complex impedance Re(f), then

$$S_{Nyquist} = 4kTRe(f)\Delta f \tag{2}$$

where now the noise may vary with frequency. It is known that the equivalent circuit of superionic cells can be expressed as a system composed of a number of series-connected resistor-capacitor parallel pairs which represent the impedance contributions of bulk electrolyte, including grain and grain boundaries in polycrystals, electrode and electrolyte-electrode interface, respectively. The impedance equation is

$$Re(f) = \Sigma R_k/(1+j\omega R_k C_k) \tag{3}$$

where R_k and C_k stand for the resistance and capacitance of the kth component in the equivalent circuit and ω is the angular frequency.

Substituting (3) into (2) we obtain

$$S_{Nyquist} = 4KT\Sigma R_k\Delta f/(1+j\omega R_k C_k) \tag{4}$$

The noise power spectrum for a single pair circuit shows f^{-2} dependence with the relaxation time equal to RC. However, the multicomponent equivalent circuit produces a superposed spectrum consisting of a number of relaxations which shows decreased frequency dependence if the resistor-capacitor parallel pairs have different, overlapping relaxation times.

Generally the Nyquist noise of a superionic system is most important at high frequencies if reversible electrodes are provided since the non-equilibrium or current noise and/or the noise arising from instrumentation may become overwhelming at low frequencies.

Nyquist noise can be used to estimate the resistance and capacitance of the materials and device. If blocking electrodes are applied, the Nyquist noise increases with decreasing frequency.

2. Diffusion noise may exist in the solid electrolyte and solution electrodes. The one-, two- and three-dimensional diffusion noise is well described by the spectrum fluctuations in the number of diffusion species[8]. The standard expressions are

$$S_{\Delta N}(f) = \langle \Delta N^2 \rangle L^2 \{1-[\exp(-\theta_1)](\cos\theta_1+\sin\theta_1)\}/D\theta_1^3 \quad (5)$$

for one dimensional diffusion, where $\theta_1=(\omega/2D)^{1/2}L$, D is the diffusion coefficient, L the effective length carrying on diffusion, N the number of diffusion species, and $\langle \Delta N^2 \rangle$ the square variance of N,

$$S_{\Delta N}(f) = -4\langle \Delta N^2 \rangle (r_0^2/D)[ber_1(\theta_2)kei_1(\theta_2)+bei_1(\theta_2)ker_1(\theta_2)]/\theta_2^2 \quad (6)$$

for two dimensional diffusion where r_0 is the radius of a cylinder which is considered in the two-dimension model, $\theta_2=(r_0^2\omega/D)^{1/2}$ and functions ber_1, kei_1, bei_1 and ker_1 are defined on Bessel functions, and

$$S_{\Delta N}(f)=12\langle \Delta N^2 \rangle r_0^2\{\theta_3^2-2+\exp(-\theta_3)[\theta_3^2(\cos\theta_3+\sin\theta_3)+4\theta_3\cos\theta_3 +2(\cos\theta_3-\sin\theta_3)]\}/D\theta_3^5 \quad (7)$$

for three-dimensional diffusion, where r_0 is the radius of a sphere concerned in a three-dimensional diffusion model and $\theta_3=2r_0(\omega/2D)^{1/2}$. At high frequencies, θ_1, θ_2 or θ_3 $>>1$, the fluctuations have an $f^{-3/2}$ spectrum. For one- and three-dimensional diffusion

$$S_{\Delta N}(f)=\alpha\langle \Delta N^2 \rangle D^{1/2}\omega^{-3/2}/L \quad (8)$$

The α in equation (8) is a constant characteristic of the dimension supposed in the diffusion model. The turnover frequency for one-, two- and three-dimensional diffusion are

$$\omega_1 = 2D/L^2$$
$$\omega_2 = D/r_o^2$$
$$\omega_3 = D/2r_o^2$$

At low frequencies where θ_1, $\theta_2 \ll 1$, the spectra vary as $\langle \Delta N^2 \rangle L/\omega^{1/2}D^{1/2}$ and $-(r_o^2/D)\langle \Delta N^2 \rangle \ell n(\omega r_o^2/D)$ respectively, and where $\theta_3 \ll 1$ the spectrum has a flat pattern as

$$S_{\Delta N}(f) = 8\langle \Delta N^2 \rangle r_o^2/5D$$

The voltage and current fluctuation spectra are

$$S(V,f) = S_{\Delta N}V^2/N^2 \tag{9}$$

and $$S(I,f) = S_{\Delta N}I^2/N^2 \tag{10}$$

If Poisson statistics are applied, we have

$$\langle \Delta N^2 \rangle = N. \tag{11}$$

Investigations on sodium and silver β"aluminas[3,4] have found that the transverse current noise shows $f^{-3/2}$ dependence and obeys the square current law, clearly indicating diffusion dominating noise. At the same time, two interesting features of the diffusion noise are observed. Firstly, the effective length carrying on diffusion is shown to be the dimension of the active sample, not the size of individual grains in polycrystals. And secondly, a large difference occurs between the numbers of the mobile ion derived from the diffusion noise expression and chemical composition. The discrepancy is attributed to strong correlation effects between mobile ions upon the generation of diffusion noise. It is interesting to note that the correlation coefficient in lead β"alumina and sodium β alumina appears smaller than sodium β"alumina, presumably because the former two substances have a smaller mobile ion distribution density.

3. Electrochemical reaction noise in superionic electrolyte cells can originate from electrolytic reactions or reactions between the solid electrolyte and electrode material or deposited electrolysis products. Simple electrochemical noise under Faradaic current without side effects can be treated as shot noise where the electrochemical reaction is described as a random sequence of non-correlated charge donation and acceptance processes[10]. However, if the contribution of the rate constant or relaxation time is taken into consideration, for single species and single relaxation time reaction the fluctuations in reaction species can be written as[2,11]

$$S_{\Delta N}(f) = 4\langle \Delta N^2 \rangle k/(k^2+\omega^2) \tag{12}$$

where k is the rate constant of the reaction.

In independent reactions, the spectrum is

$$S_{\Delta N}(f) = \Sigma S_{\Delta N,x} = 4\Sigma\langle \Delta N_x^2 \rangle k_x/(k_x^2+\omega^2) \tag{13}$$

Instead, for complex or multi-stepped reactions, the fluctuation spectrum of reaction species is determined by the relation between the individual reactions. Similarly, equations (9)-(11) are applied to derive voltage and current fluctuations for the reaction noise.

In β"alumina and Nasicon cells, f^{-2} noise is observed at newly prepared contacts or in the presence of current. Moreover, in the absence of current but in the state of chemical non-equilibrium a noise spectrum related to equations (12) and (13) can also be observed under appropriate experimental conditions. If I=kNe is assumed, the reaction noise is written as[3]

$$S(V,f) = 4Nk^3e^2Z^2/(k^2+\omega^2) \tag{14}$$

where e is electronic charge and Z the effective impedance of the contact. The application of equation (14) has succeeded in estimating

the rate constant of the reaction at the non-equilibrium sodium β"alumina/ mercury and amalgam contacts[3,9].

4. Multicomponent noise. Equations (1-2), (4)-(8), (12) and (13) define the electrical fluctuations of Nyquist, diffusion and simple and independent reaction noise. When a Faradaic current passes through a superionic cell, several ionic processes are involved. They are electrochemical reactions in anodic and cathodic compartments, charge transfer between electrode and electrolyte, and ion transport through the solid electrolyte membrane and ionic electrode. The resulting noise is composed of all the individual noise generation terms:

$$S_{total} = S_{Nyquist} + S_{reaction} + S_{diffusion} \tag{15}$$

Certain noise components may dominate in a specified frequency or current range. Transitions from one noise state to another usually produce slope changes or discontinuities in the noise spectrum plots.

In practical measurements, the turnover frequency of a particular noise may be at very low frequencies, far below the experimental frequency range. Then diffusion and reaction noise expressions (8) and (12) can be simplified to equations (16) and (17),

$$S_{diffusion}(V,f) = \kappa_{diffusion}\omega^{-3/2} \tag{16}$$

$$\text{and } S_{reaction}(V,f) = \kappa_{reaction}\omega^{-2} \tag{17}$$

where $\kappa_{diffusion}=\alpha D^{1/2}V^2L^{-1}N^{-1}$ and $\kappa_{reaction}=4kV^2N^{-1}$. Equations (16) and (17) can be used to fit observed noise spectra even though the characteristic constants of the system under observation are unknown.

5. Noise decay. Excess Noise existing in a non-equilibrium system or an equilibrated system due to external perturbation decreases with time as the system goes forward to equilibrium or the perturbation is released. The noise decay concerned here can be

thought to behave like a relaxation process. It has been found that such decay of noise in the superionic system can be usually represented by an exponential time equation although the decaying noise may be generated by different mechanisms.

NOISE MEASUREMENT

Two different procedures are used to measure the noise of superionic cells. The first is the analog method in which noise signals are entered into a preamplifier and filter assembly. Then the amplified and filtered fluctuation voltages at a given measurement bandwidth are converted into a d.c. voltage and measured by a digitial voltmeter. The other procedure used involves FFT digital analysis. The output signals from the preamplifier are analyzed using an A/D conversion and FFT program on a computer system. The set up[12] accurately measures the Nyquist noise of resistances from 10^4 to $2x10^8$ Ω over the frequency range 10^{-3} to $1x10^4$ Hz. Block diagrams of the noise measurement systems are given in Figure 1.

Lock-in techniques can be helpful in measuring low frequency noise levels with high sensitivity since the lock-in technique suppresses preamplifier 1/f noise. The method has succeeded in determining the resistance fluctuations of hydrogen diffusion in niobium films[13].

Two- and four-terminal cells are prepared for noise examinations. The former measures noise generated in the electrode and solid electrolyte as well as at the interfaces of two phase contacts. Noise measured at transverse electrodes of the four terminal cell, however, eliminates interfacial and electrodic effects and mainly collects the noise accompanying ionic processes in the bulk electrolyte membrane. Therefore a comparison of transverse noise with the noise collected at a two-terminal cell or from the longitudinal electrodes of a four-terminal cell allows us to distinguish the noise in bulk solid electrolyte, electrode and at electrolyte-electrode interface. The electrodes used in noise measurement cells may be reversible or

blocking in nature. Different electrode configurations containing uncommon mobile ions to the solid electrolyte may be applied to the detection of the noise associated with interdiffusion in electrolyte and ion exchange between electrolyte and electrode material. In addition, observations on non-equilibrium contact noise is also carried out at newly prepared contacts or under shifted equilibrium state by external electrical or chemical perturbation. The relaxation to equilibrium is registered after given periods of storage time.

Log-log noise power spectra plots often given clear frequency dependence relations. Other types of noise plots, such as equivalent resistance, equilivalent current and noise-times-frequency against frequency plots are also found helpful in an understanding of the nature of noise in particular cases.

SIMULATION AND ANALYSIS OF MULTICOMPONENT NOISE

Different combinations of multicomponent noise are calculated by inserting relevant parameters into equations (2), (4), (5)-(7), (12) and (13), as shown in Figures 2 and 3. In a multicomponent noise system, the ideal spectrum is modified if superposed noise components exist. Separation of such overlapped noise patterns into individual noises in some cases is possible by using either graphic or analytical methods. As shown in Figure 2, discontinuities originate from the transitions between the diffusion and reaction type noise or between noises of similar types but having different relaxation times.

On the other hand, it has been known that the continuous distribution of relaxation times may lead to a continuous noise spectrum with decreased frequency dependence. The noise plot for a series of independent chemical reactions having closely distributed rate constants is exemplified in Figure 3(a). It is also seen from Figure 3(b) that the log(f)-log(SXf) plot can be useful to disclose the multiple nature of the heavily superposed noise.

SOME RESULTS OF SUPERIONIC NOISE STUDIES

1. Contact and current noise in sodium β"Al_2O_3 cells with different ion electrodes.

As shown in previous investigations[3,14], low noise contacts can be established between a sodium β"alumina electrolyte membrane and sodium amalgam or NaI propylene carbonate electrodes. These electrodes are reversible in nature.

On the other hand, only quasi-equilibrium contacts are found in cells with aqueous electrodes or solution electrodes which contain uncommon, exchangeable ions to the sodium β"alumina membrane. The noise in excess of equilibrium noise shows a f^{-2} spectrum and is most likely attributed to an ion exchange reaction between the β"alumina and contacting electrode material. Figure 4 illustrates such noise arising from silver nitrate in glycerine and calcium bromide in propylene carbonate and aqueous sodium nitrate solution electrodes to Naβ"alumina. It can be seen that the noise level increases in the sequence of $Ag^+ > Na^+ + H_3O^+ > Ca^{2+}$. The ion exchange noise relaxes very slowly and is observable even after several months' storage.

Both diffusion and reaction dominated current noise are found in the cells in the presence of current, as shown in Figure 5. Inserting relevant parameters into equations (5-8), (12) and (13) enables us to fit the noise spectrum pattern and estimate the interdiffusion and chemical reaction properties of different ions in sodium β"alumina. The high current noise associated with the aqueous and $CaBr_2$ electrodes seems to suggest sodium ion diffusion. Interestingly the f^{-2} noise found in the two-terminal silver nitrate glycerine cell can be fitted to two independent reactions with rate constant $k=4\times10^3$ and $k<10^{-2}sec^{-1}$.

2. Noise decay. Establishment of equilibrium of quasi-equilibrium contact noise in the sodium β"alumina cells with common or

uncommon ion electrodes at room temperature involves a slow-aging process. The aging time ranges from some ten minutes to hours, depending upon the species as well as the concentration of electrode material. Dilute solutions usually need longer aging periods. The excess noise decays exponentially with time. The aging effect may be thought to be associated with the formation of an equilibrated or a quasi-equilibrated interface between β"alumina electrolyte and the solution electrodes. A diffuse double layer is expected to spread over both sides of β"alumina and ion electrode contact since an interface permeable to mobile ions is present. A number of noise decay patterns are exemplified in Figure 6.

Illustrated in Figure 7 are noise spectra measured during the recovery time of a heavily polarized mercury/β"alumina/mercury cell[9]. The noise decays according to a time exponential equation. The relaxation time calculation gives a diffusion coefficient of 1.8×10^{-6} cm^2/sec thus indicating sodium ion diffusion.

3. Degradation accompanying noise. High noise levels sometimes accompanied by temporary fluctuations of charging current are detected during charging a NaI(propylene carbonate)/β"alumina/NaI(propylene carbonate) cell at current densities >900 $\mu A/cm^2$ or temporarily >3700 $\mu A/cm^2$ at room temperature. Sometimes the frequency dependence of noise decreases. After that the β"alumina is discolored. This particular high current noise may be likely attributed to the degradation of β"alumina electrolyte. A typical noise spectrum showing a f^{-1} pattern is illustrated in Figure 8.

Figure 9 presents a noise spectrum showing a relaxation plateau which is obtained after a degradation test. It is reasonable to suspect that the noise relaxation arises from the sodium ion depleted layer on the β"alumina surface resulting from electrolytic degradation. Considering that the capacitance of the electrically insulating layer is shunted by the input impedance of preamplifier, therefore we can estimate the capacitance about 10^{-9} Farad, equivalent

to an insulating layer thickness of tenths of μm. Alternatively the noise relaxation pattern can be explained by a combination of diffusion and reaction noise. The turnover frequency calculated based on diffusion noise suggests an effective length of about four μm, which may be assumed to be related to the thickness of the sodium ion depletion layer on the β"alumina.

4. Noise in Nasicon cell. In general, with Nasicon it is easier to form low noise contacts with sodium iodide propylene carbonate or aqueous sodium nitrate electrodes than in the case of Naβ"alumina. Low noise contacts are established in relatively short aging times, as seen in Figure 6. Excess noise is found in the aqueous contact at low frequencies, indicating a reaction between Nasicon and the aqueous solution. Unlike for β"alumina, no diffusion noise is detected in the presence of current. Using the diffusion noise expression and the diffusion constant estimated from the Nernst-Einstein relation, we may explain the low diffusion noise in Nasicon by supposing a small correlation effect owing to the lower density of mobile sodium ions in the three-dimensional Nasicon structure.

Current noise in both longitudinal and transverse contacts, Figure 10, shows f^{-2} noise spectra, indicating chemical reaction noise, but the noise levels in the longitudinal contact are greater. Higher current noise than that predicted from the square current law is found as the current density increases to high values. In addition, high contact noise developed at high charging current persists for more than ten hours. Both the high current noise and prolonged post current noise are assumed to arise from degradation of the Nasicon. As for Naβ"alumina, the color of the Nasicon electrolyte changes to greyish after high current noise generation. After degradation the Nyquist noise increases slightly, probably because of the increase in resistance due to loss of mobile sodium ions during electrolysis as well as chemical reactions between Nasicon and deposited sodium.

5. Temperature dependence of noise. The temperature dependence of noise at high and low frequencies in the superionic systems reflects thermal activation energies associated with the bulk resistance, ion transport and reaction properties. The activation energy determined at 5000 Hz is 0.30, 0.18 and 0.21 eV for sodium β"alumina, β alumina and Nasicon, respectively, which is in agreement with the conductivity activation energies. However the low frequency activation energy is more complicated since it is affected by variations in ionic correlation and ion transport and reaction kinetics. The activation energies determined at 10 Hz is 0.16, 0.3 and 0.5eV, respectively. Figure 11 presents activation energy plots for several materials.

CONCLUSIONS

Investigations of conductivity fluctuations in various β"alumina single crystals and ceramics have indicated[1,3-5,9] that the noise in superionic systems can be described by Nyquist, diffusion and chemical reaction noises and therefore the noise spectrum measurement provides an approach to evaluate the transport and chemical reaction behavior in the bulk superionic material and at interfacial contacts. Recent investigations on sodium β"alumina and Nasicon ceramics lead to the following conclusions:

1. Non-equilibrium or quasi-equilibrium reaction noise is found in the cells composed of sodium β"alumina electrolyte and uncommon, exchangeable ion electrodes. The reaction noise attributed to the ion exchange reactions at the electrolyte-electrode interface increases in the sequence of $Ag^{+}>Na^{+}+H_3O^{+}>Ca^{2+}$ electrode.

2. Diffusion and reaction noise has been confirmed in Naβ"alumina/$AgNO_3$(glycerine) and $CaBr_2$(PC) cells.

3. Excess noise present in newly prepared cells or after external perturbations decays exponentially with time.

4. The degradation of β"alumina and Nasicon electrolyte leads to abnormally high noise levels. Sometimes the frequency dependence decreases to f^{-1}.

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FIGURE CAPTIONS

Figure 1. Block diagram of (a) analog and (b) digital noise measurement systems.

Figure 2. Multicomponent noise simulation showing discontinuity in slope due to transitions between different noise sources.

Figure 3. Simulation of multicomponent reaction noise having closely distributed rate constants.

Figure 4. Excess contact noise at $AgNO_3$(glycerine), $CaBr_2$(propylene carbonate) and aqueous $NaNO_3$ electrodes to Naβ"alumina.

Figure 5. Current noise in Naβ"alumina/Na amalgam, $AgNO_3$(glycerine), $CaBr_2$(propylene carbonate) cells: (a) Na amalgam, transverse contact noise[3]; (b) $AgNO_3$(glycerine), longitudinal contact noise, solid lines are the fits to Nyquist and reaction noise; and (c) $CaBr_2$(propylene carbonate), longitudinal(L) and transverse(T) contact noise, solid lines are the fits to Nyquist, diffusion and reaction noise(L) and Nyquist and diffusion noise(T), respectively.

Figure 6. The noise decay pattern in β"alumina and Nasicon cells: β"alumina/$AgNO_3$ saturated in glycerine; 0.7 M $CaBr_2$ in propylene carbonate; 0.01 M, 0.1 M, 1 M aqueous $NaNO_3$; 0.5 M NaI in propylene carbonate; Nasicon/0.5 M NaI in propylene carbonate.

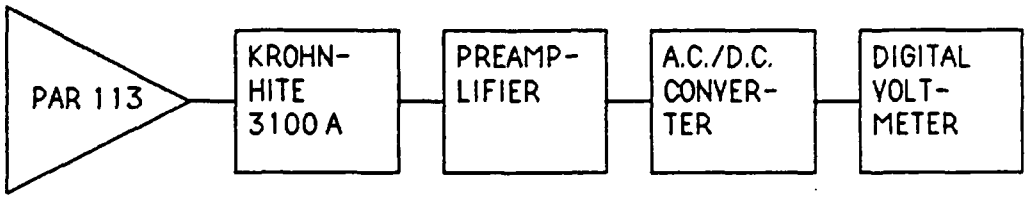
Figure 7. Current noise spectrum and post current noise spectrum in mercury/sodium β"alumina/mercury cell[9].

Figure 8. Abnormally high current noise and f^{-1} spectrum of NaI(propylene carbonate)/Naβ"alumina/NaI(propylene carbonate) cell at high current densities.

Figure 9. Spectrum showing noise relaxation plateau after degradation test of NaI propylene carbonate/Naβ"alumina/aqueous $NaNO_3$ cell, fitted with diffusion and reaction noise.

Figure 10. Current noise in a Nasicon cell[6].

Figure 11. Noise activation energy plots of superionic materials[3,6].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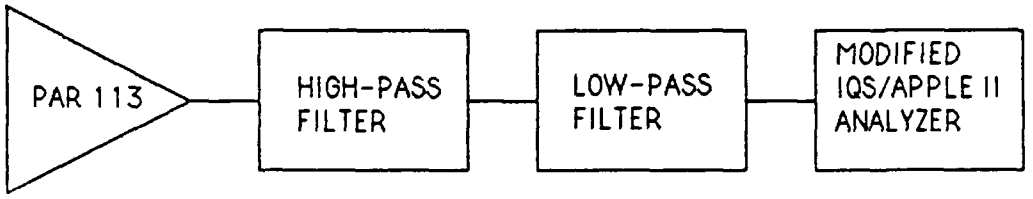
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Figure 1

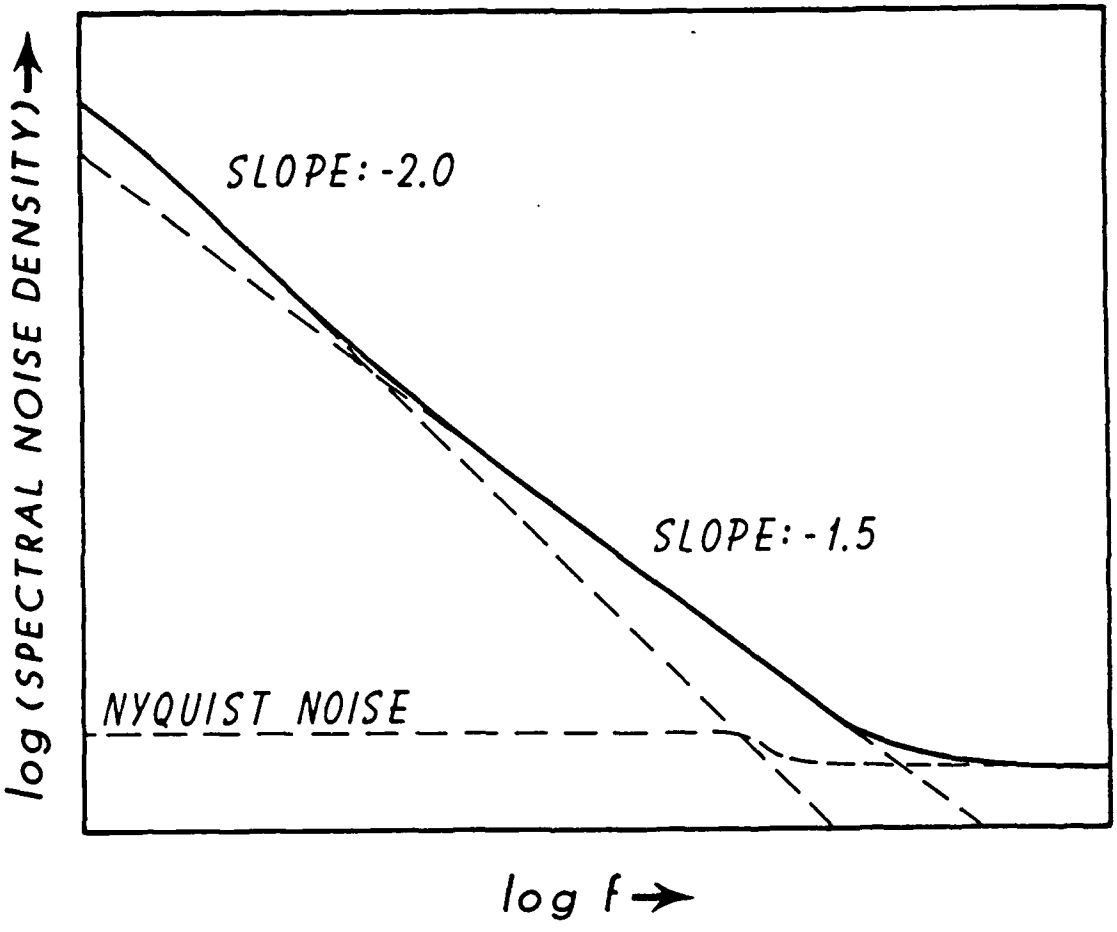
log (SPECTRAL NOISE DENSITY)
SLOPE: -2.0
SLOPE: -1.5
NYQUIST NOISE
log f

Figure 2(a)

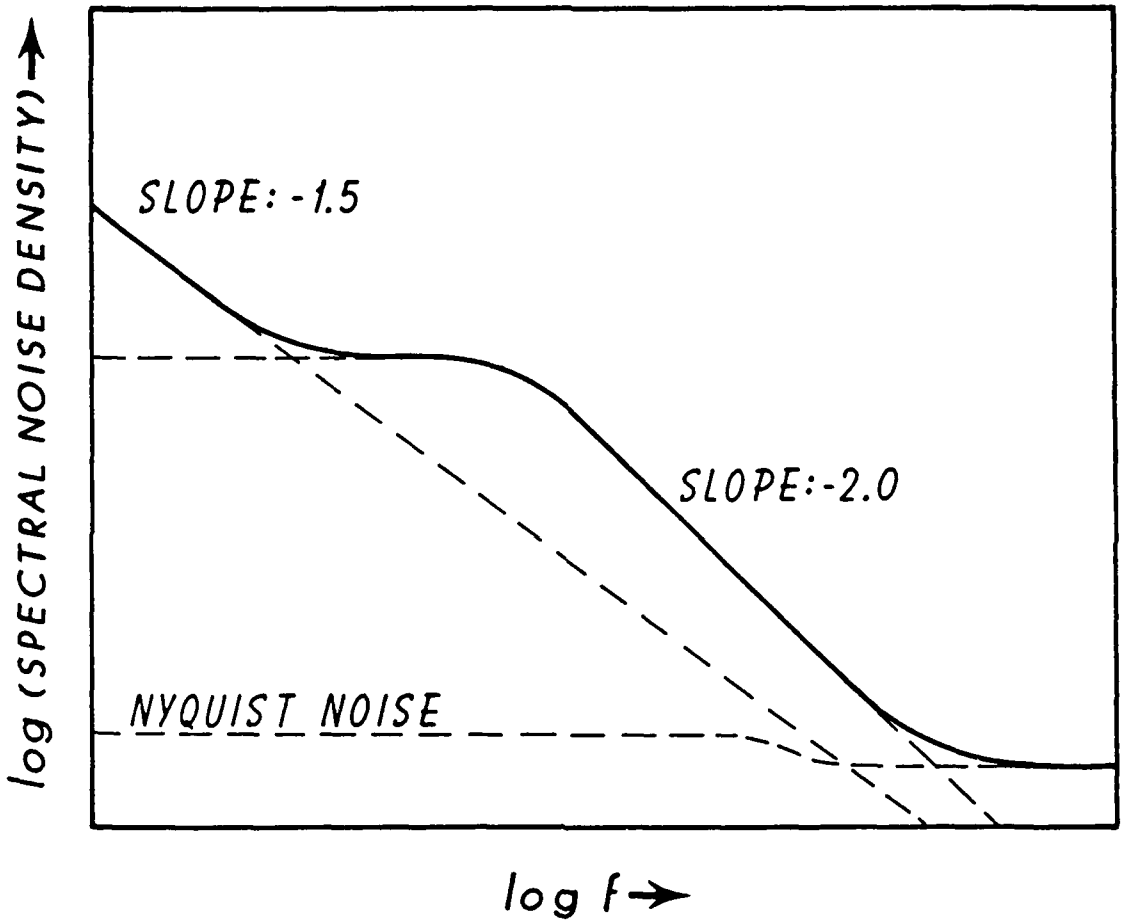
log (SPECTRAL NOISE DENSITY)
SLOPE: -1.5
SLOPE:-2.0
NYQUIST NOISE
log f

Figure 2(b)

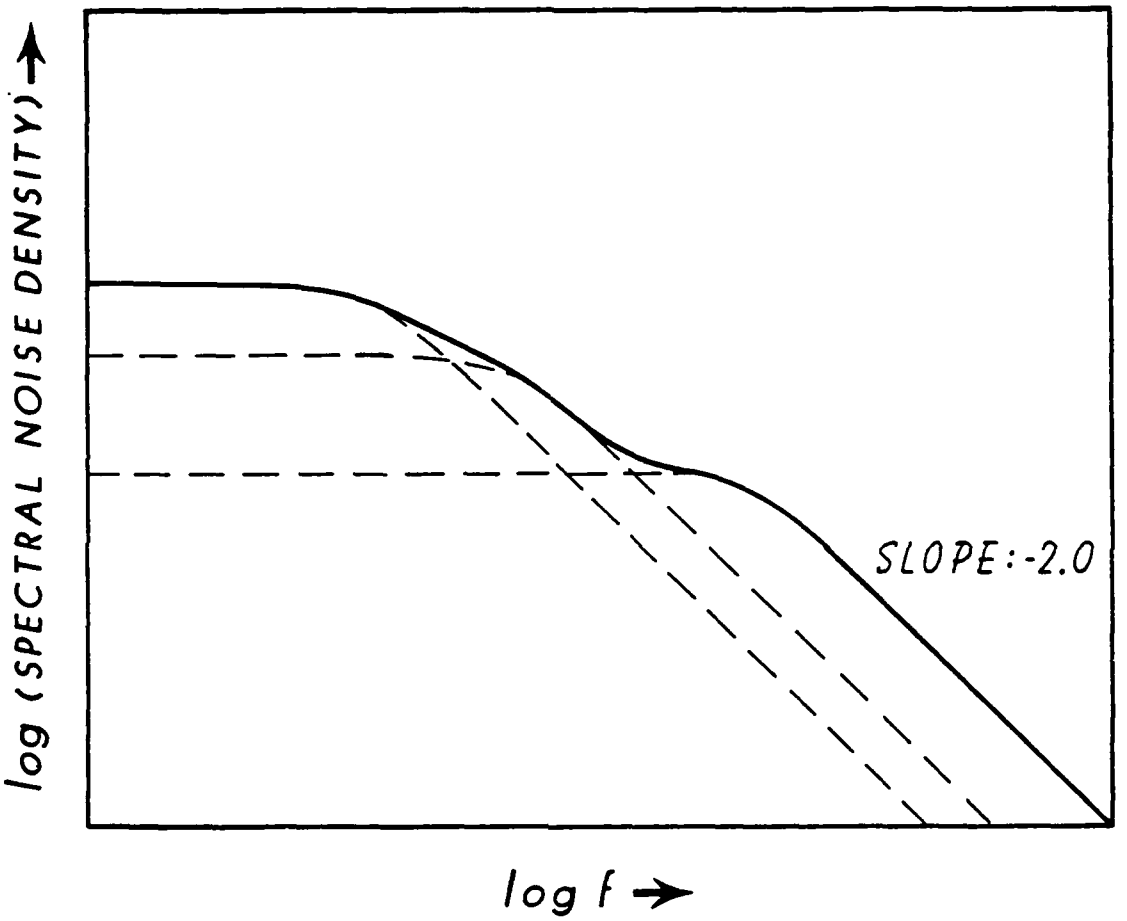

Figure 2(c)

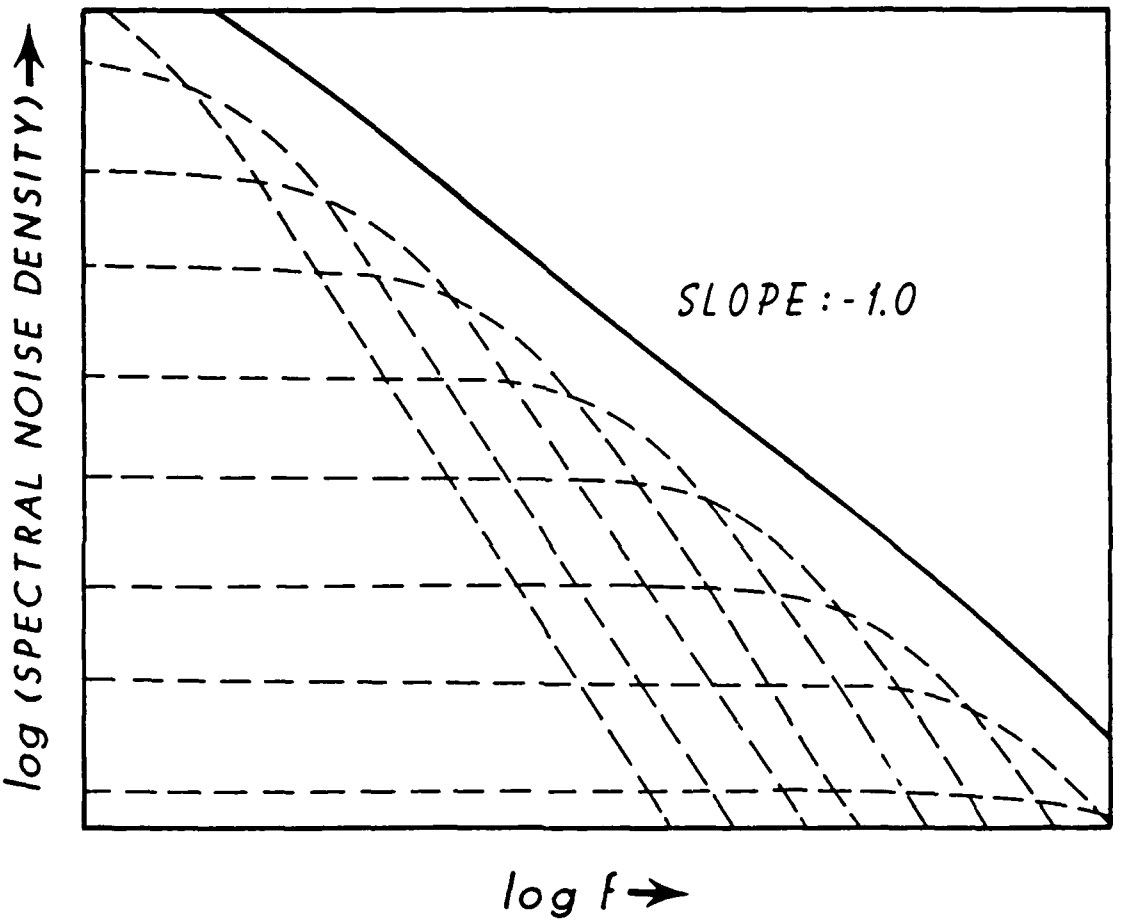

Figure 3(a)

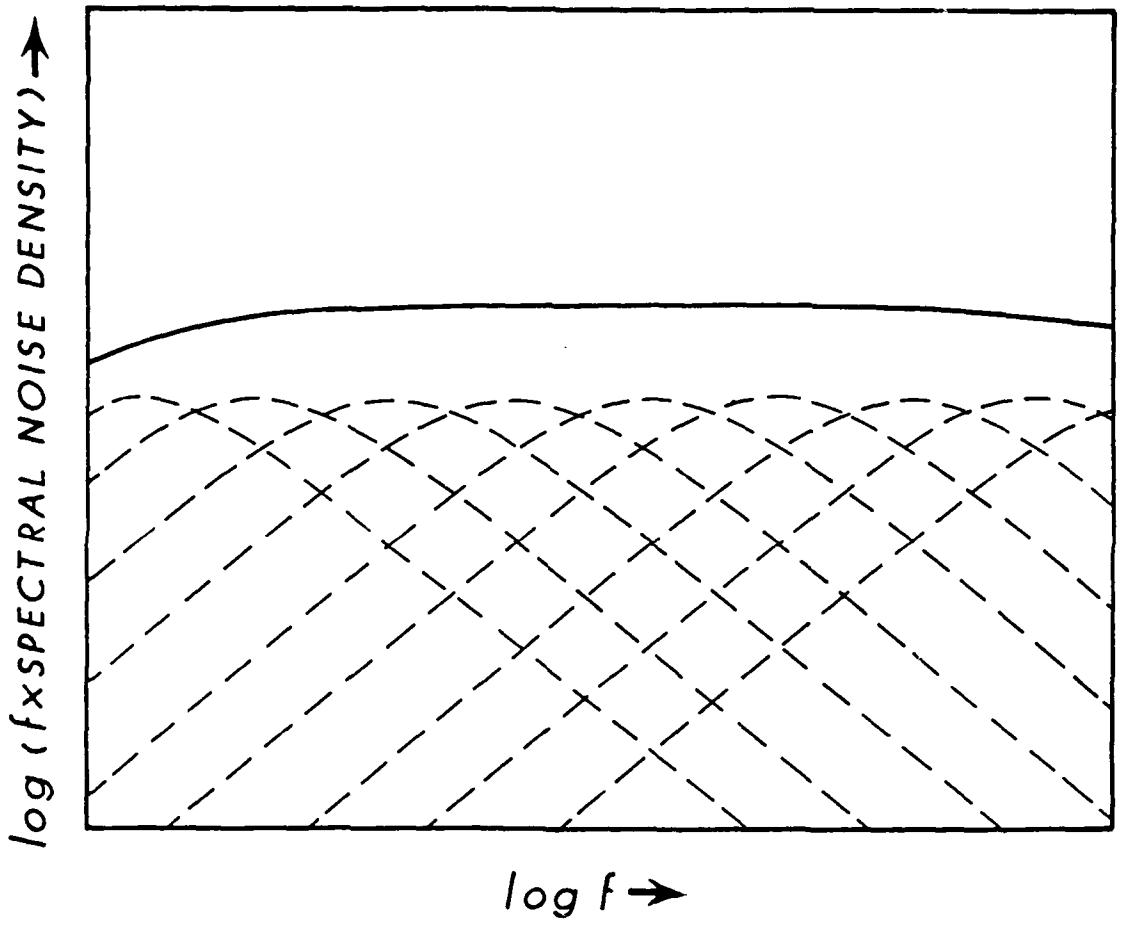

Figure 3(b)

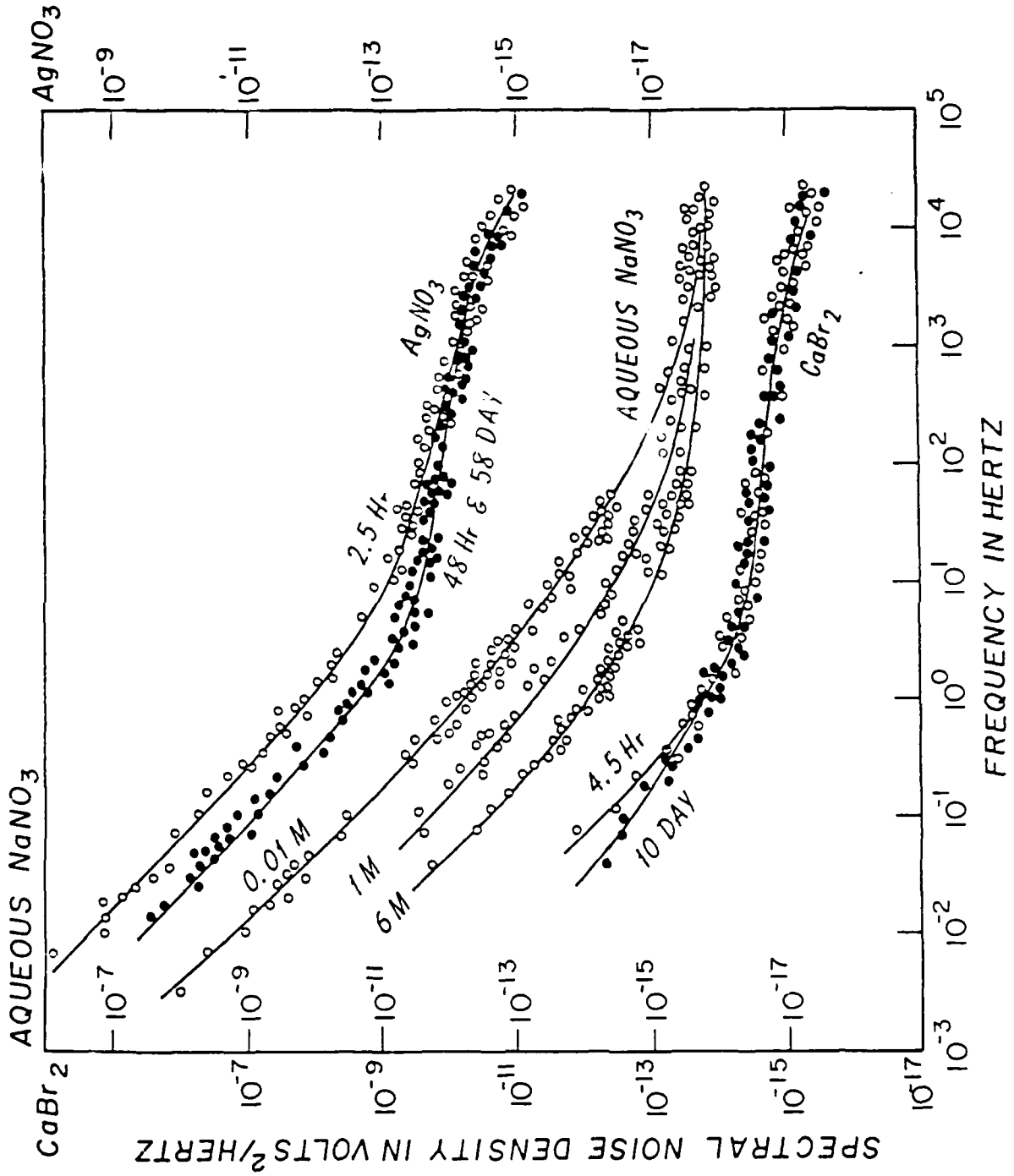
AgNO3
AQUEOUS NaNO3
CaBr2
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
2.5 Hr
48 Hr & 58 DAY
0.01 M
1 M
6 M
4.5 Hr
10 DAY
AgNO3
AQUEOUS NaNO3
CaBr2

Figure 4

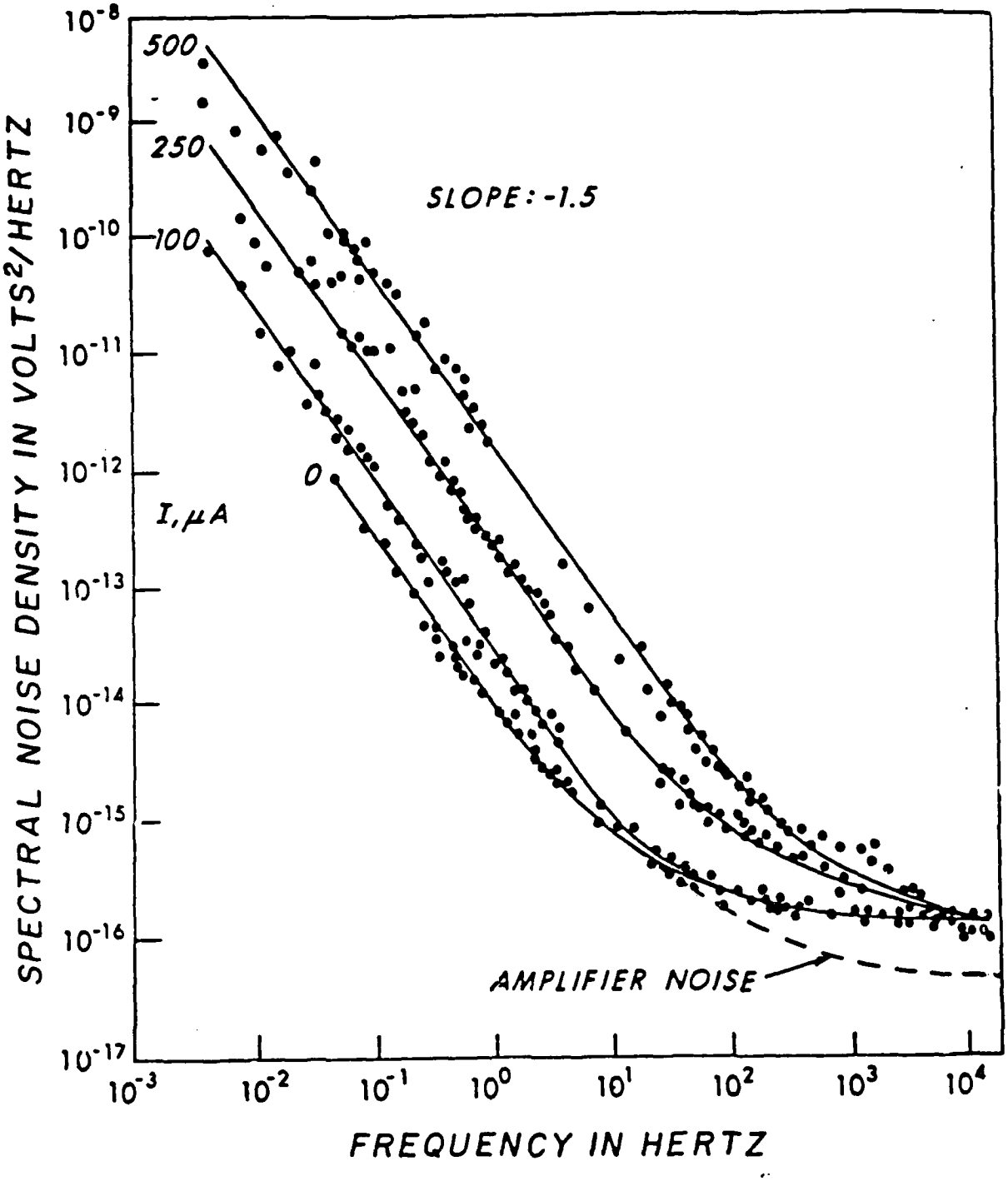
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
SLOPE: -1.5
500
250
100
0
I, μA
AMPLIFIER NOISE
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴

Figure 5(a)

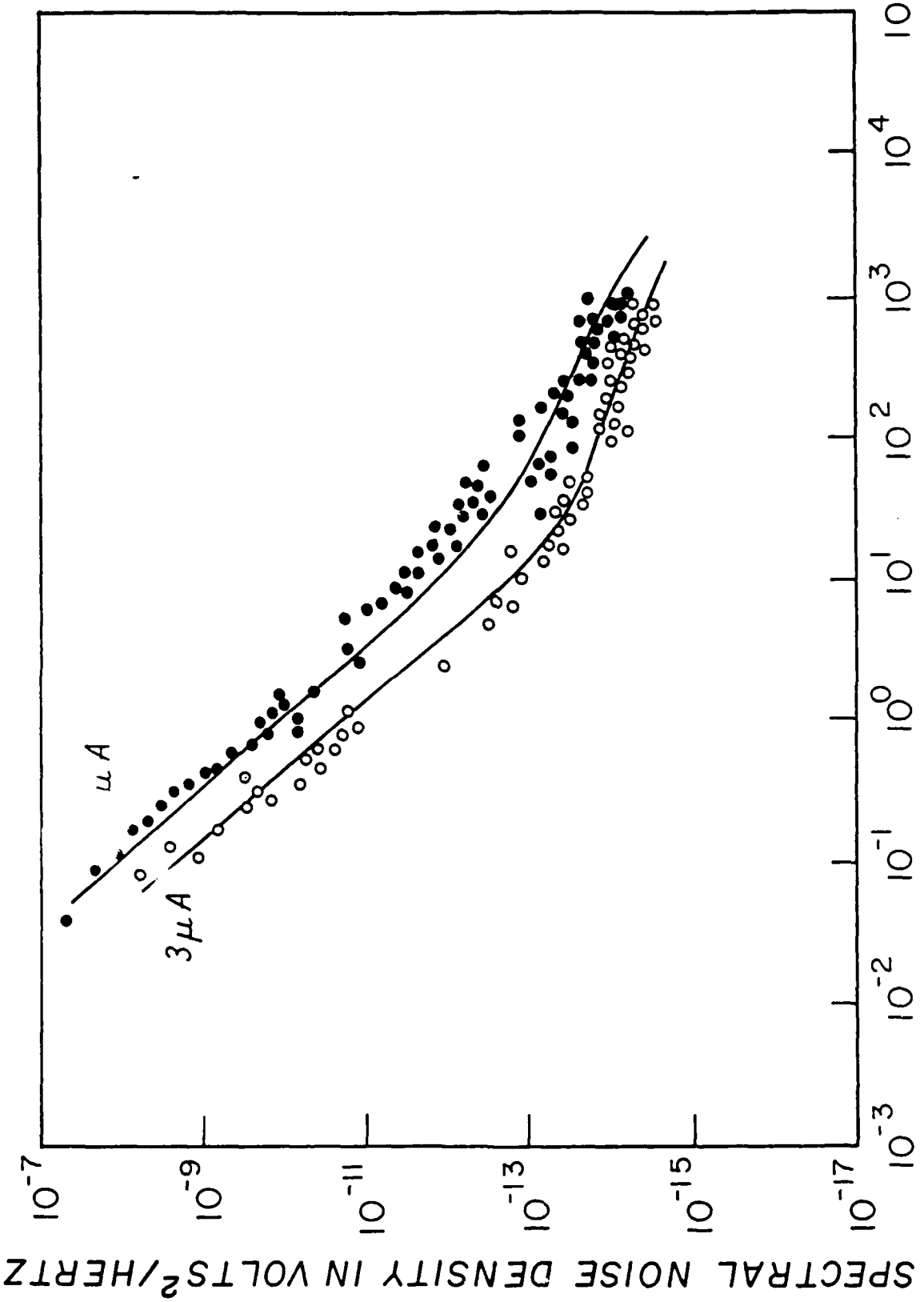
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
FREQUENCY IN HERTZ
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
1 μA
3 μA

Figure 5(b)

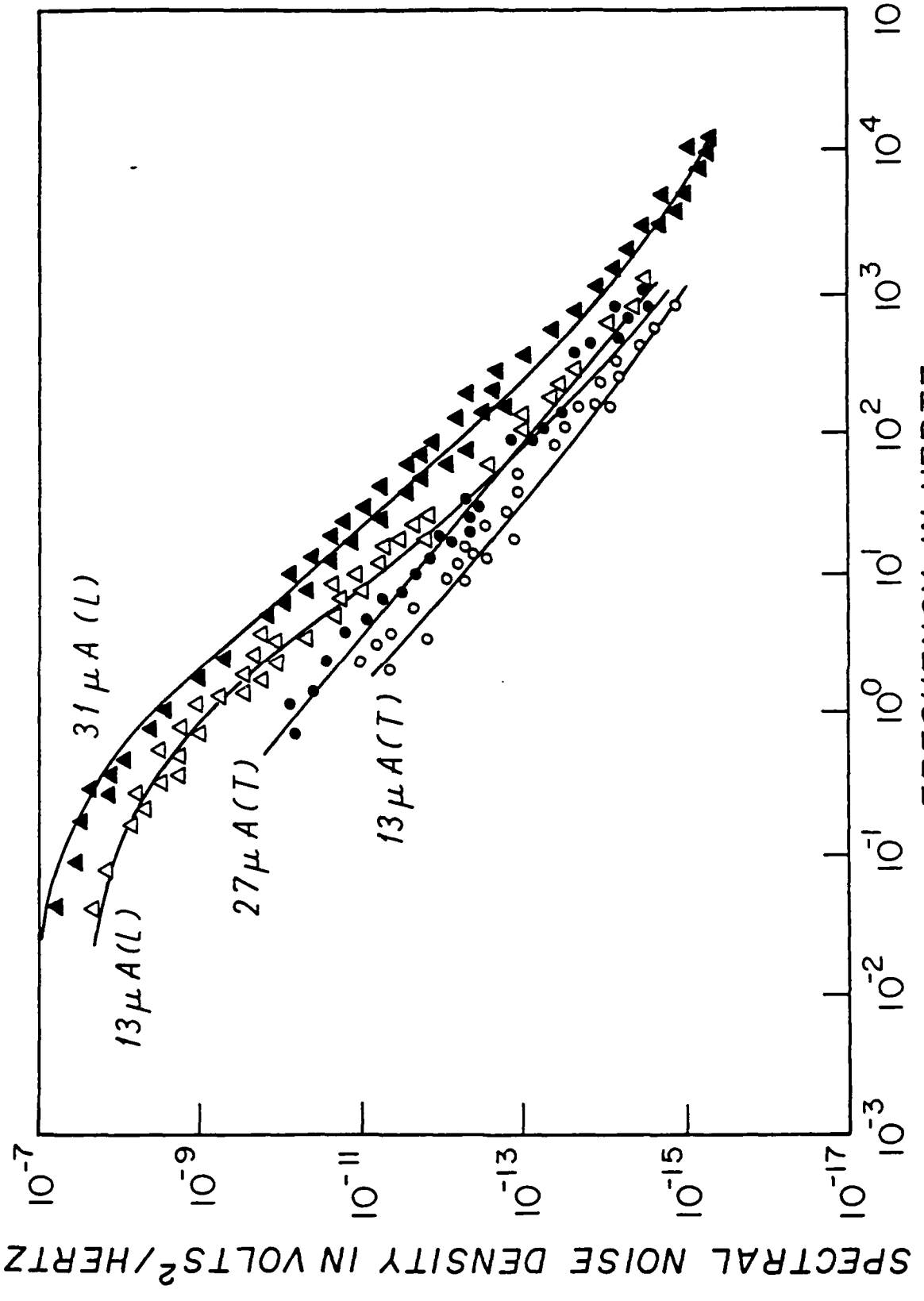
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
31 μA (L)
13 μA (L)
27 μA (T)
13 μA (T)
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵

Figure 5(c)

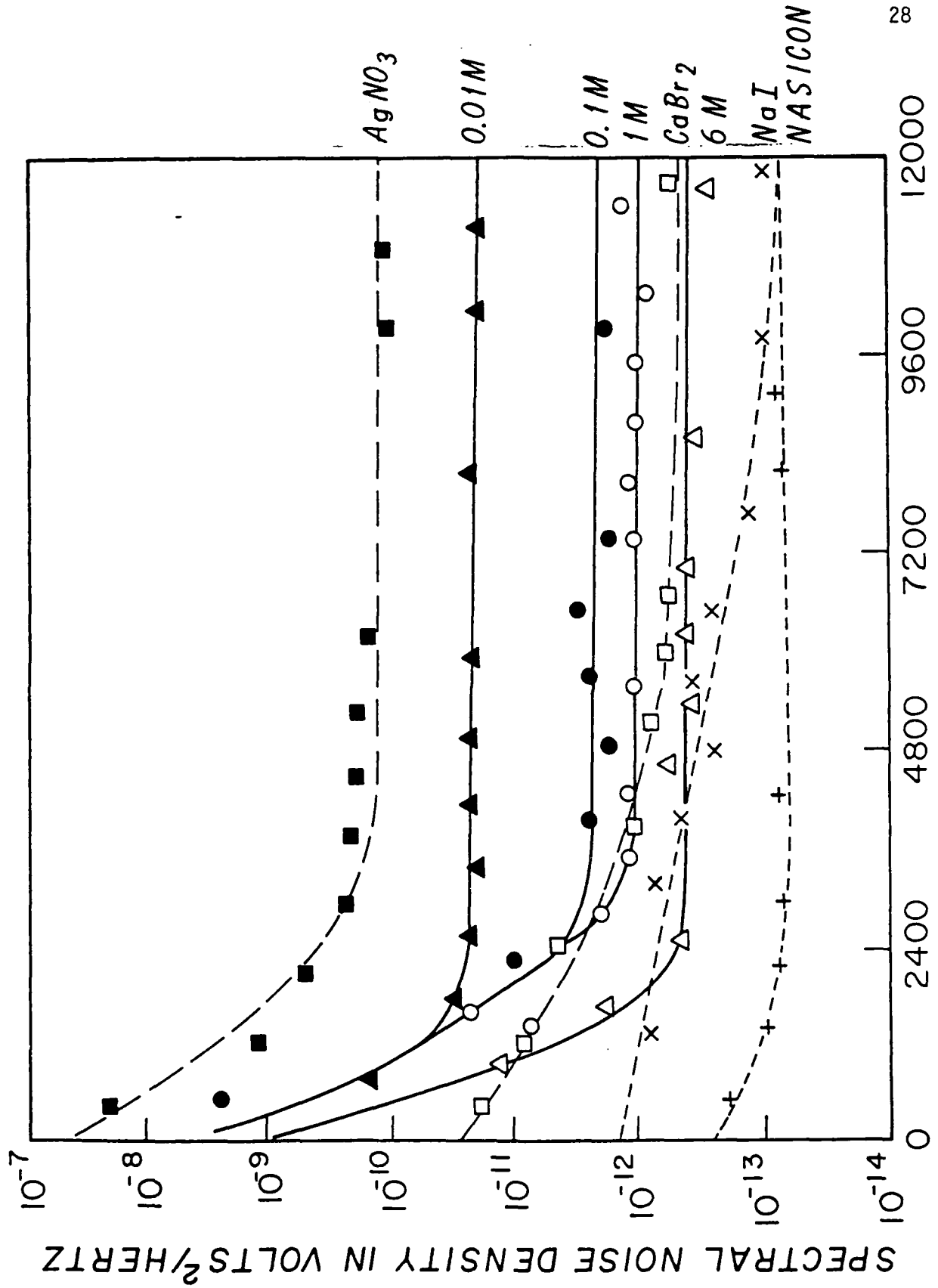
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
0
2400
4800
7200
9600
12000
TIME (sec)
AgNO₃
0.01M
0.1M
1M
CaBr₂
6M
NaI
NASICON

Figure 6

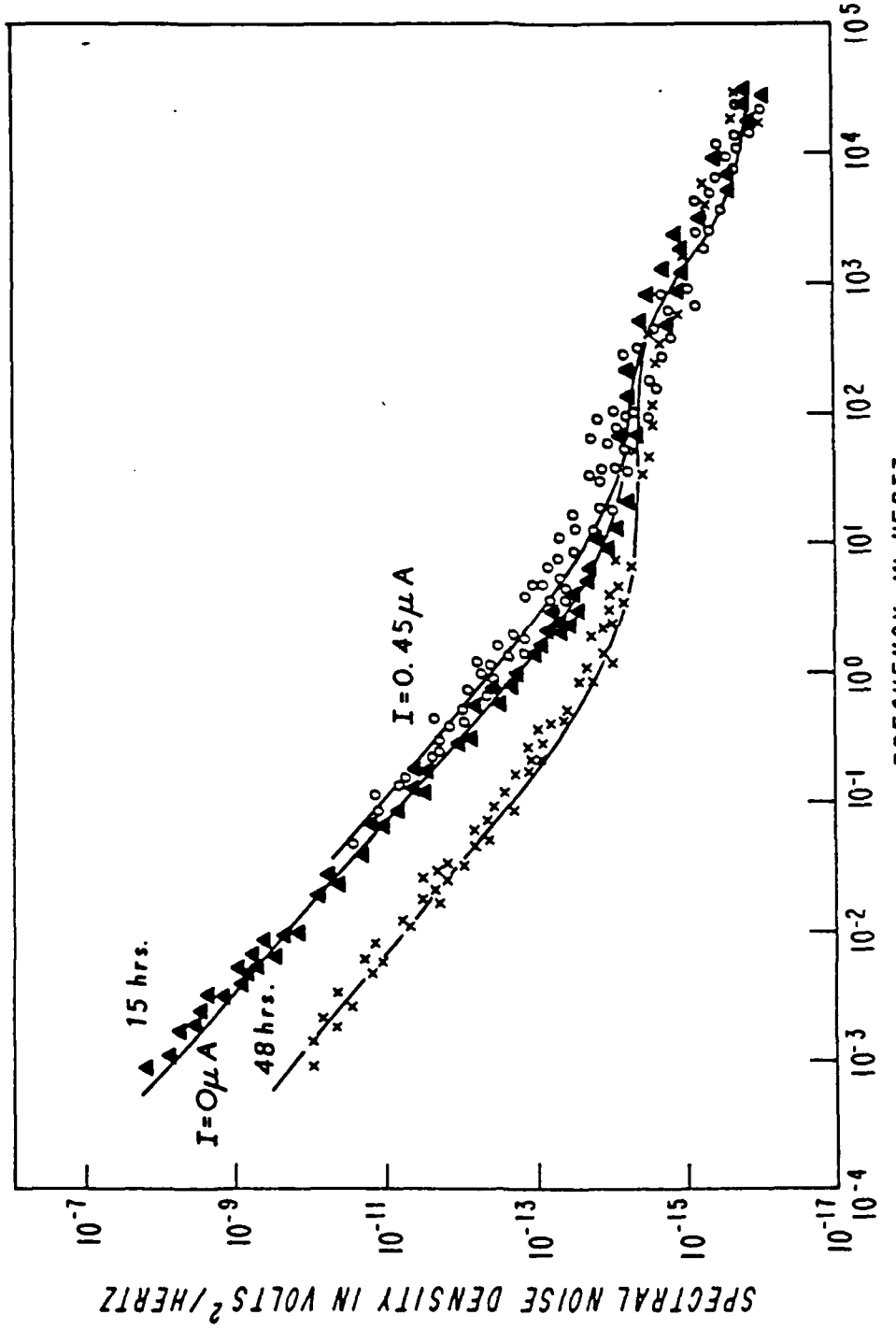
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
I=0μA
15 hrs.
48 hrs.
I=0.45μA
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻⁴
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵

Figure 7

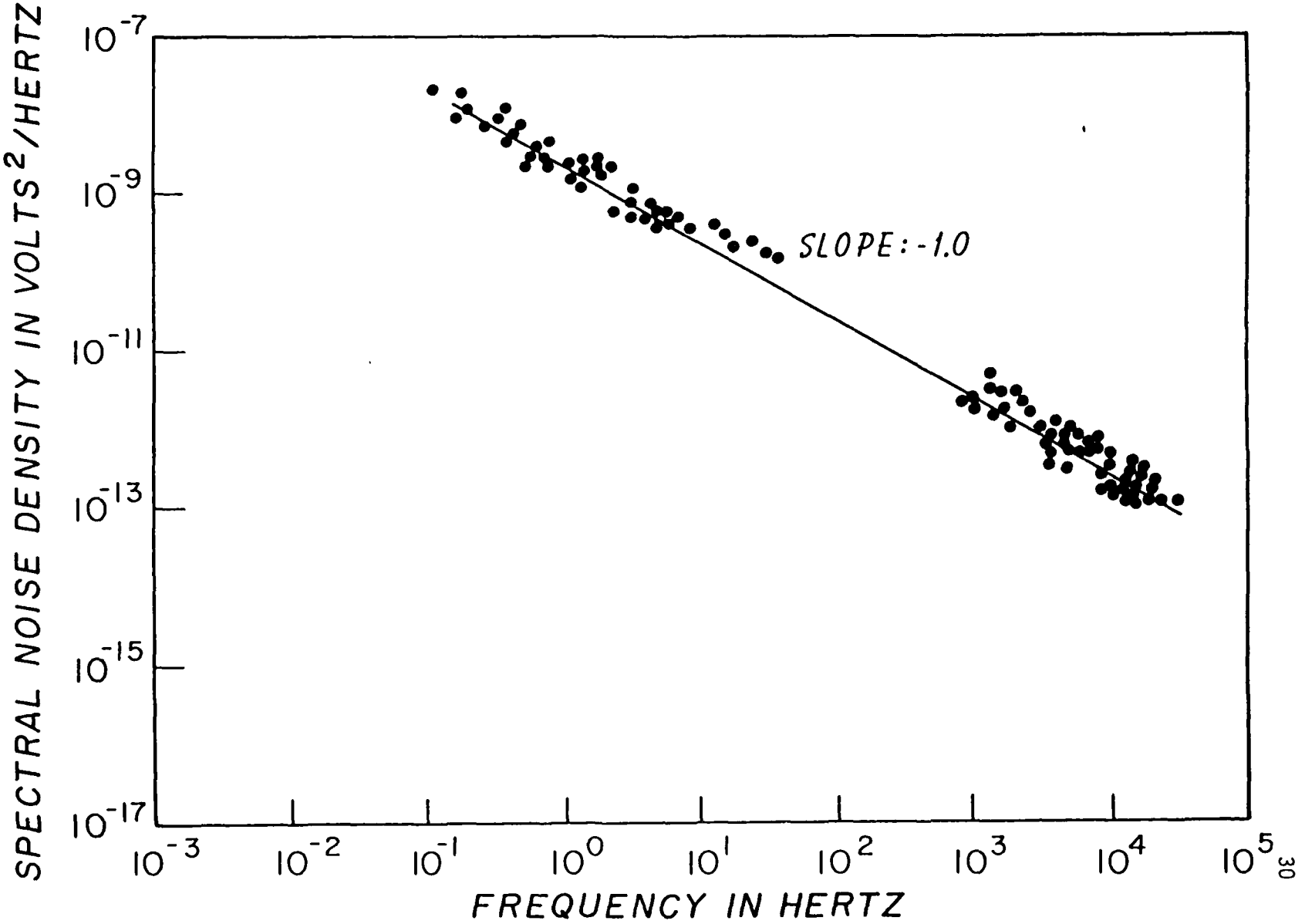
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
SLOPE: -1.0
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
FREQUENCY IN HERTZ

Figure 8

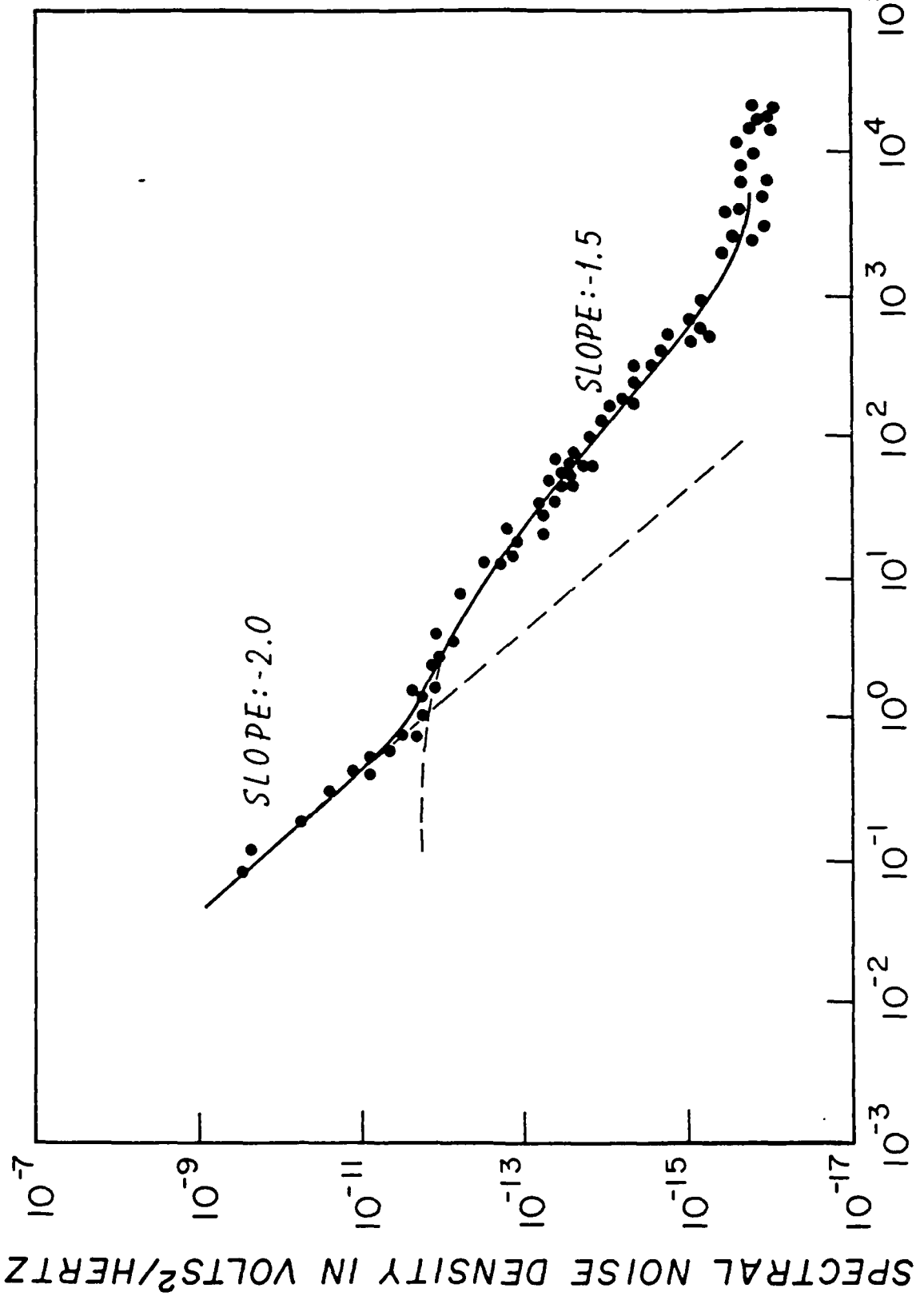
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
SLOPE:-2.0
SLOPE:-1.5
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵

Figure 9

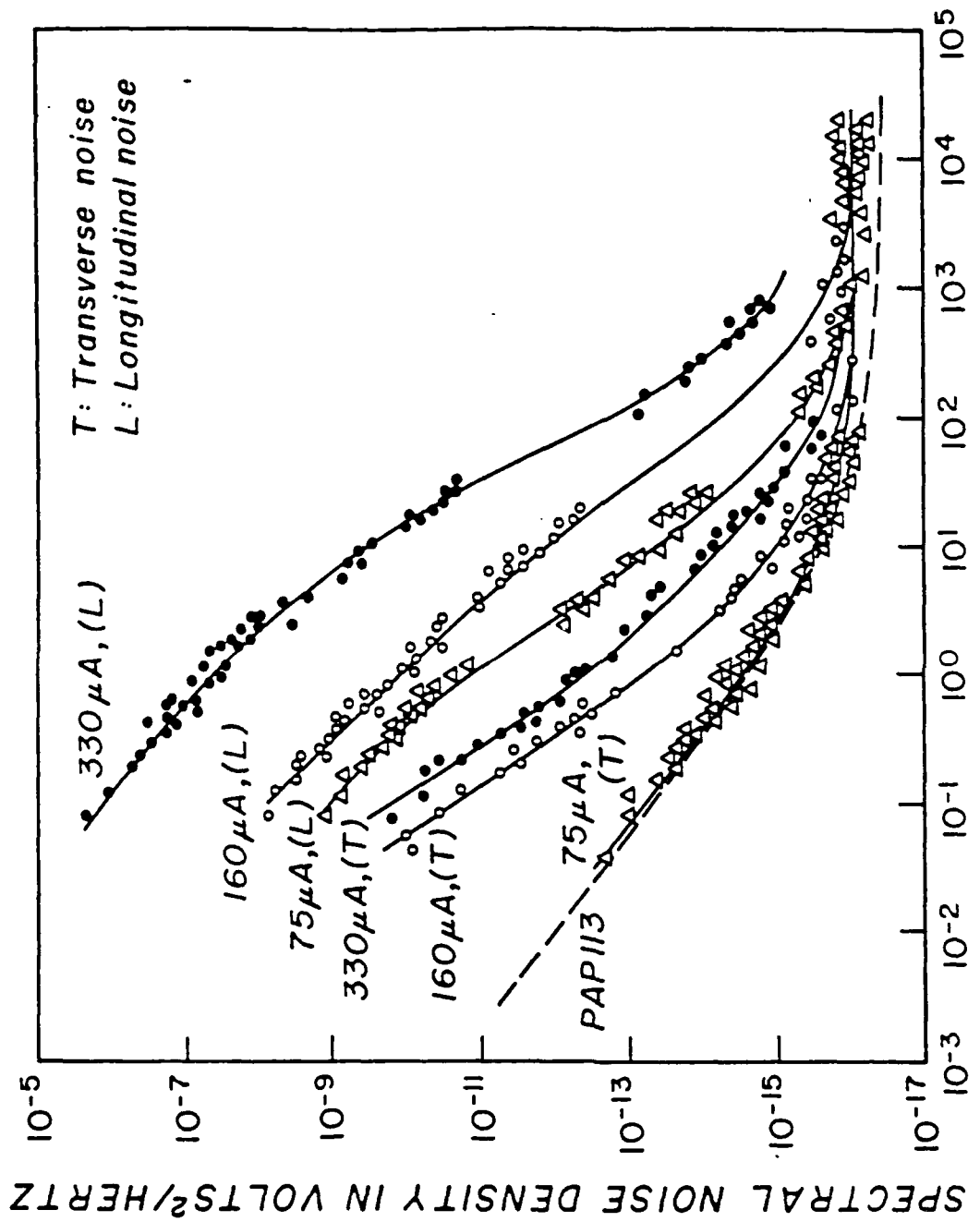
T: Transverse noise
L: Longitudinal noise
330μA,(L)
160μA,(L)
75μA,(L)
330μA,(T)
160μA,(T)
75μA,(T)
PAP113
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
10⁻⁵
10⁻⁷
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵

Figure 10

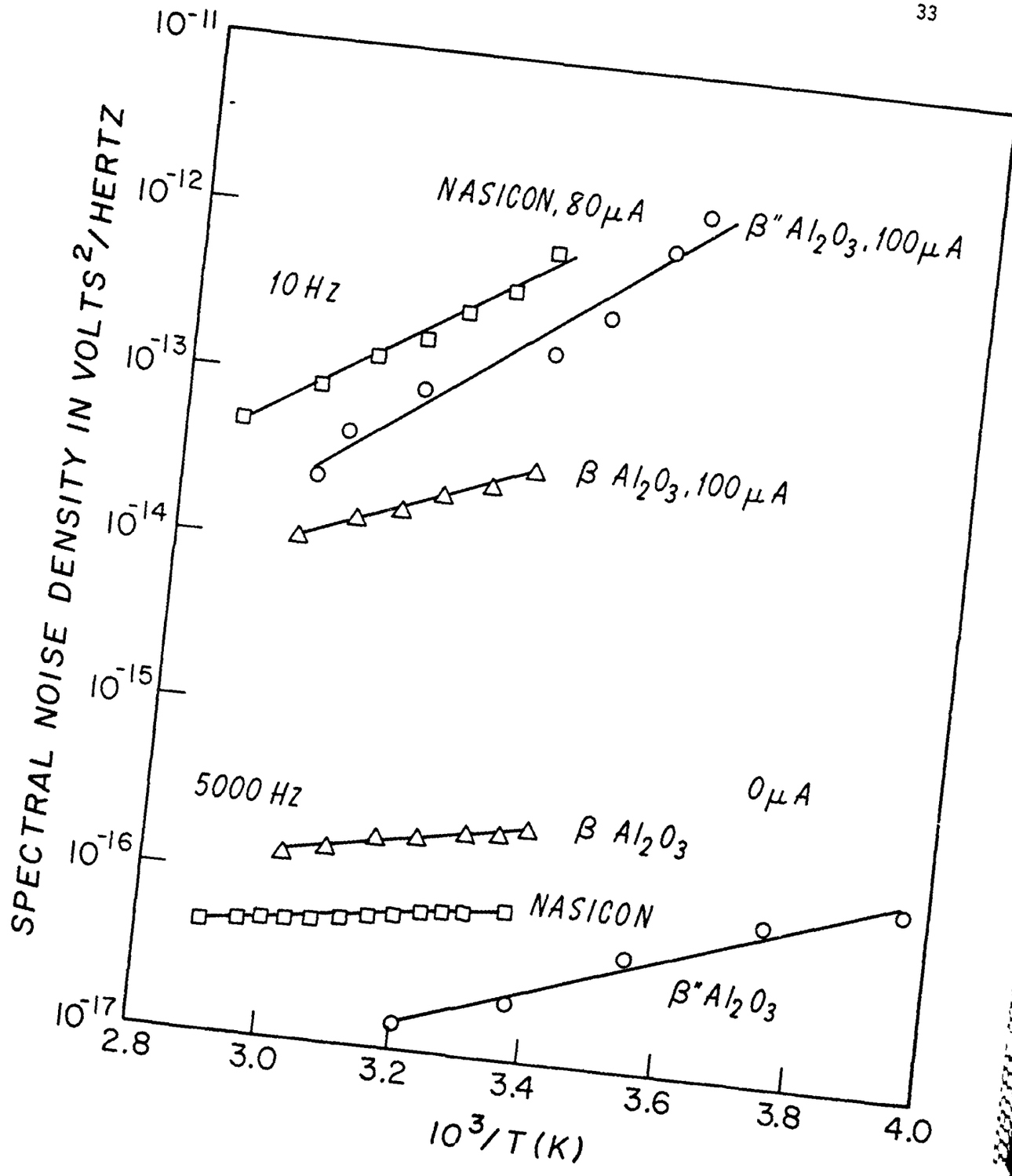
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
NASICON, 80μA
β"Al₂O₃, 100μA
10 Hz
β Al₂O₃, 100μA
5000 Hz
0μA
β Al₂O₃
NASICON
β"Al₂O₃
2.8
3.0
3.2
3.4
3.6
3.8
4.0
10³/T(K)

Figure 11